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G1B BAA BCC

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GB 2018679 A

GB 1511286 A

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(58) Field of Search

UK CL (Edition O) G1A AKA, G1B BAA BBC BBG BCC

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Online: WPI, Claims, Japio, Analytical Abstracts

(54) **Explosives detection**

(57) Test samples of energetic material, especially explosives, are heated under reduced pressure below 20mbar and light emission, particularly chemiluminescent emission, measured to indicate presence of explosive. A photomultiplier or photodiode may be used for measurement. Heating is to e.g. 300 - 500deg.C. Apparatus for the detection has a heated chamber with one of its walls transparent to light, pumps for keeping the chamber under a reduced pressure, a detector for emitted light measurement and a sample port.

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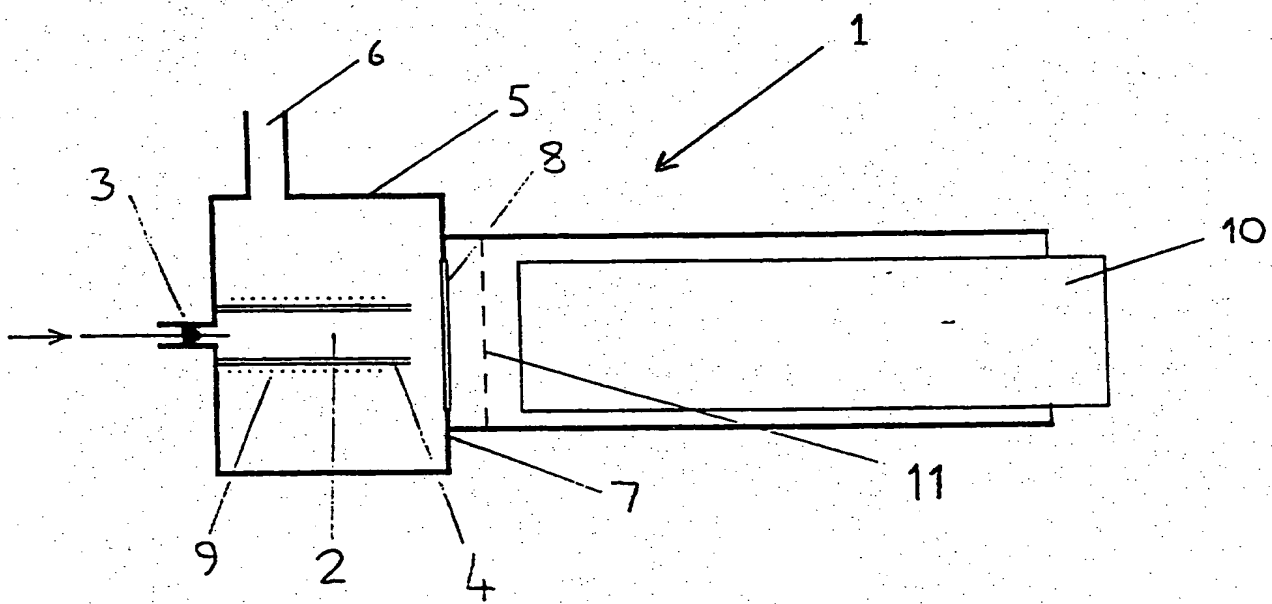


Figure 1

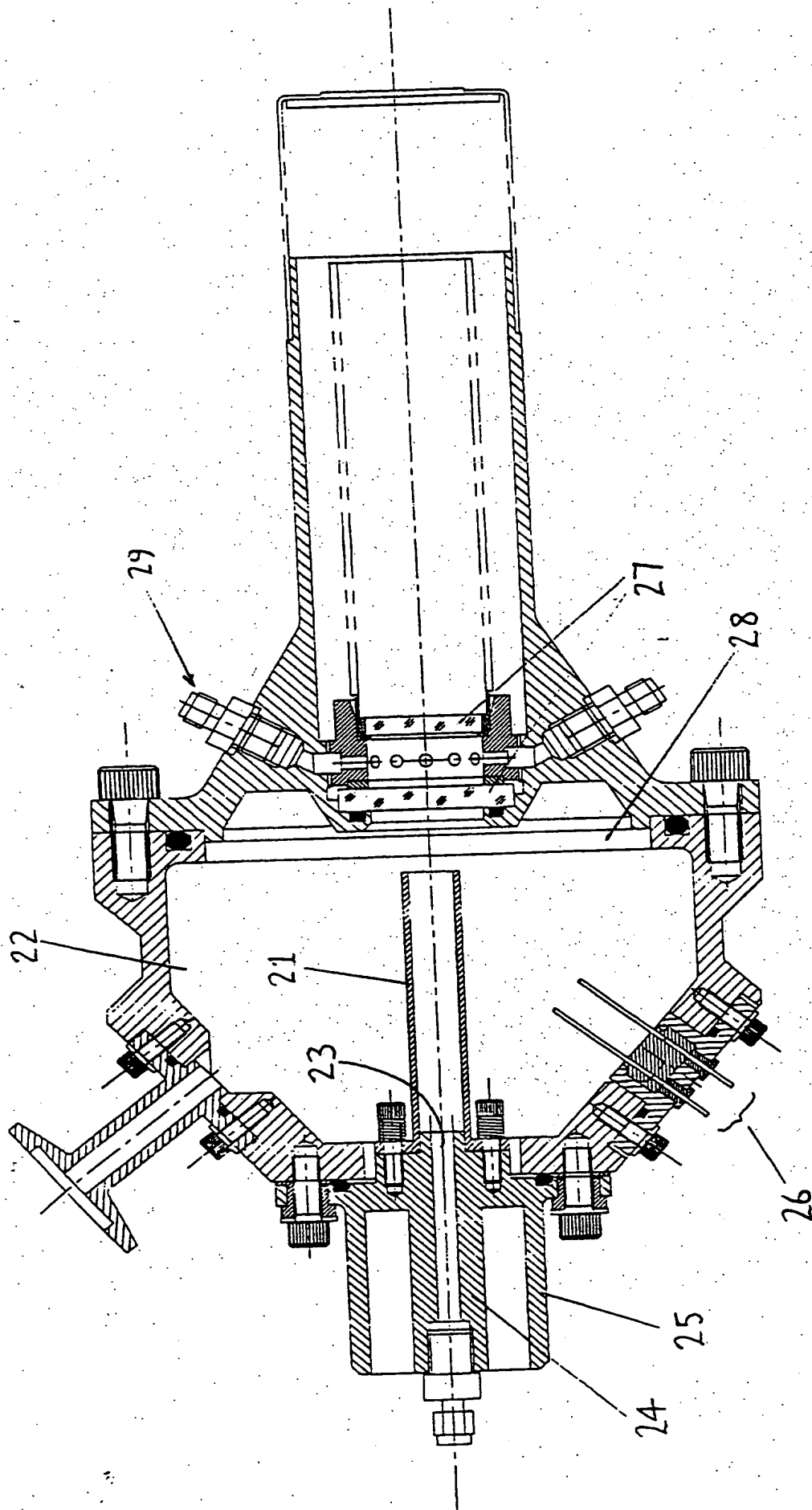


Figure 2

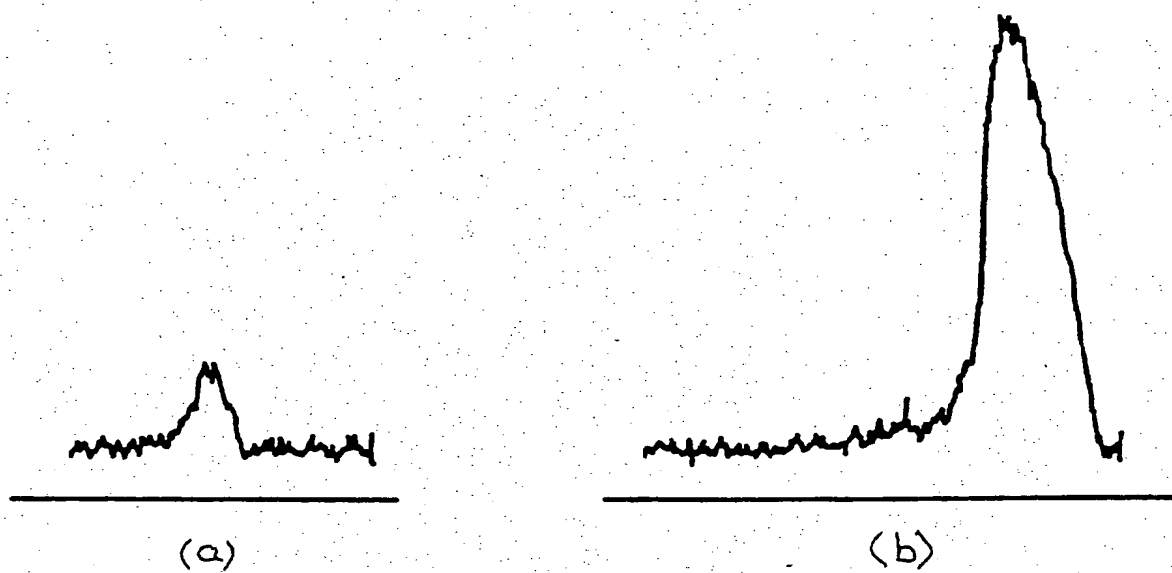


Figure 3

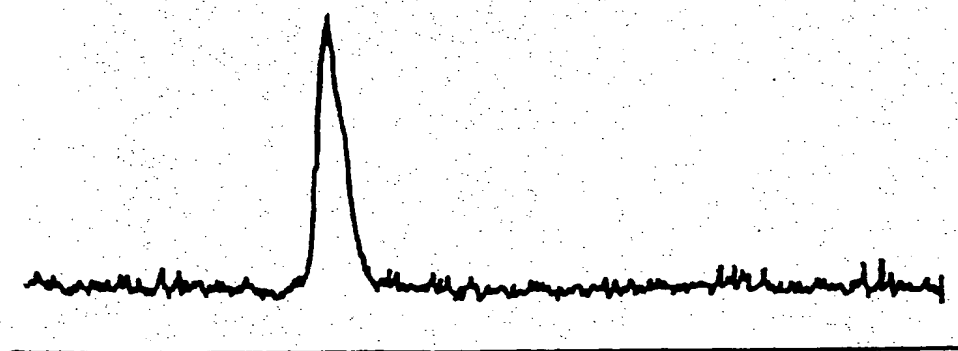


Figure 4

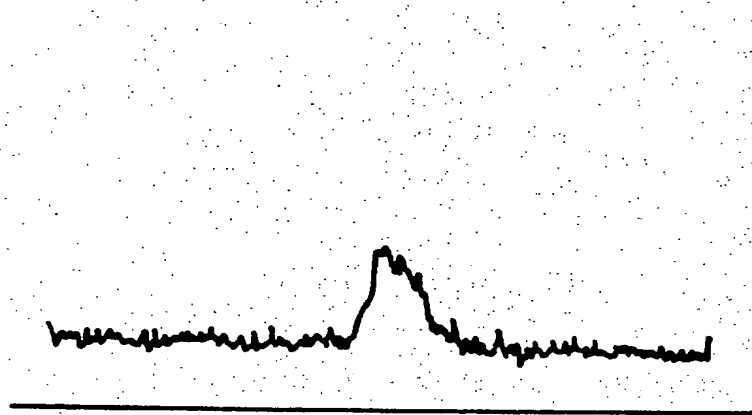


Figure 6

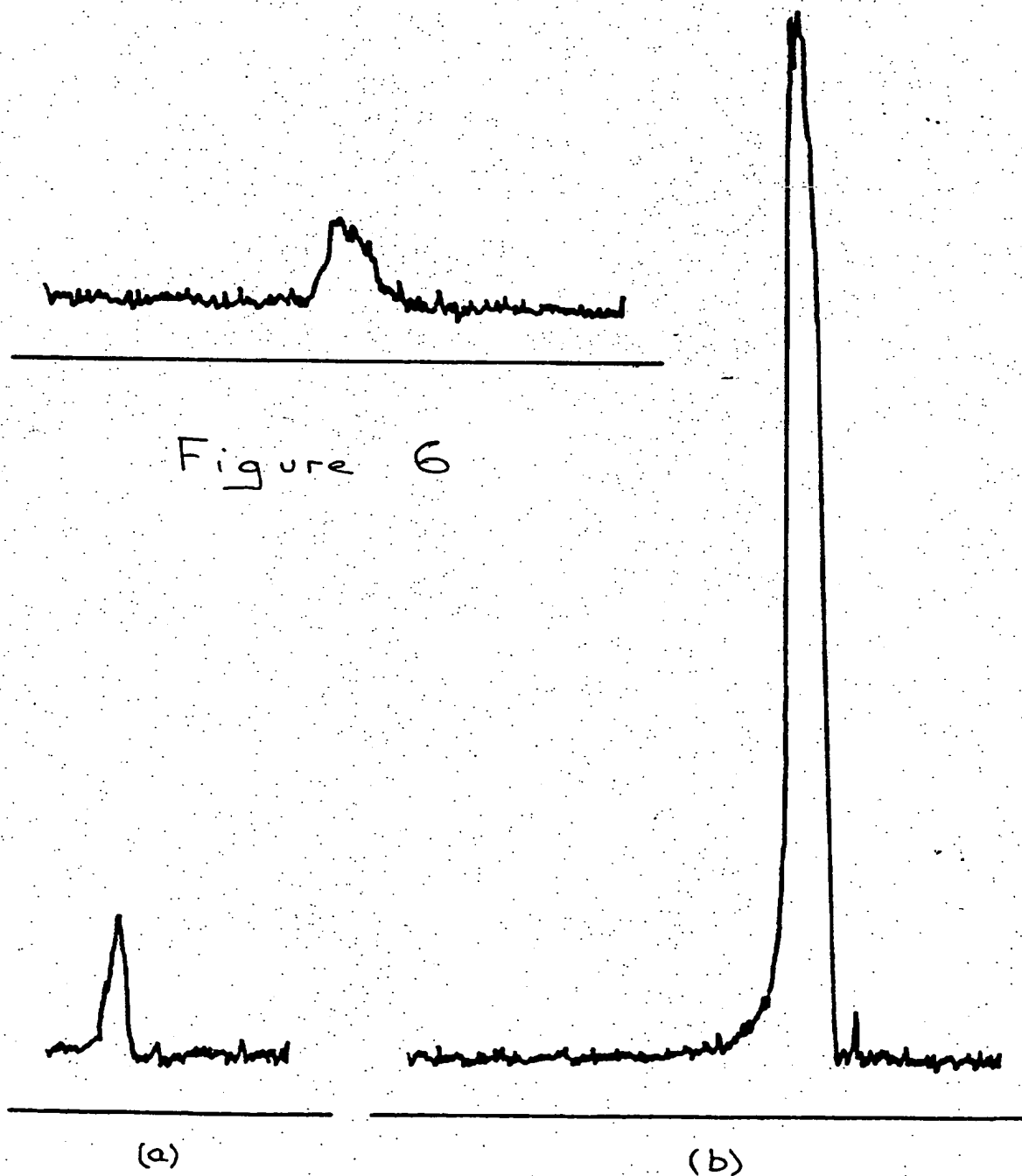


Figure 5

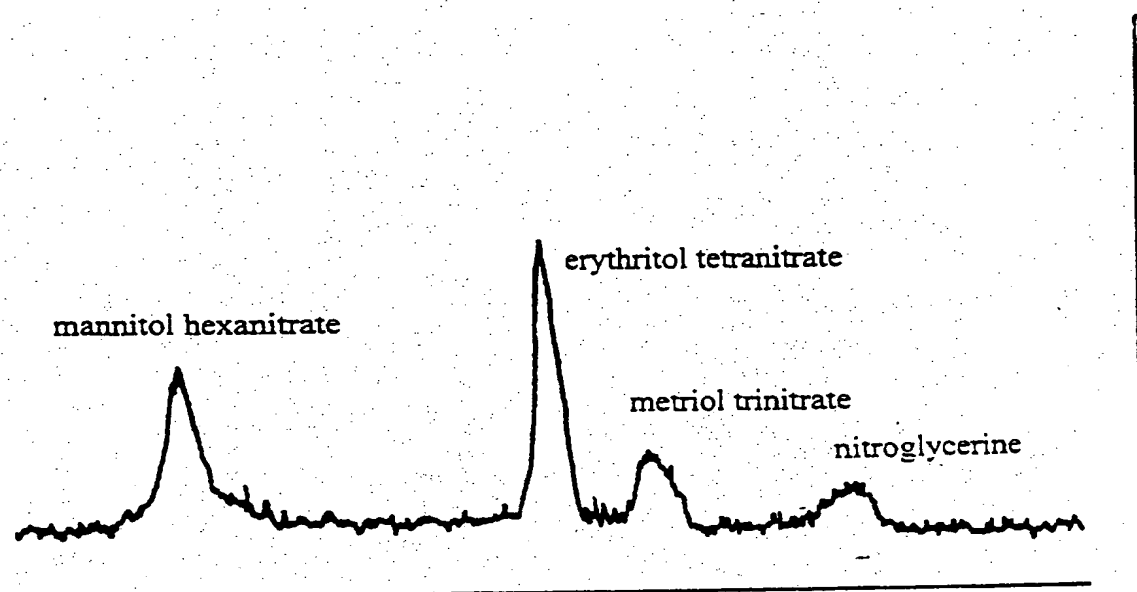


Figure 8

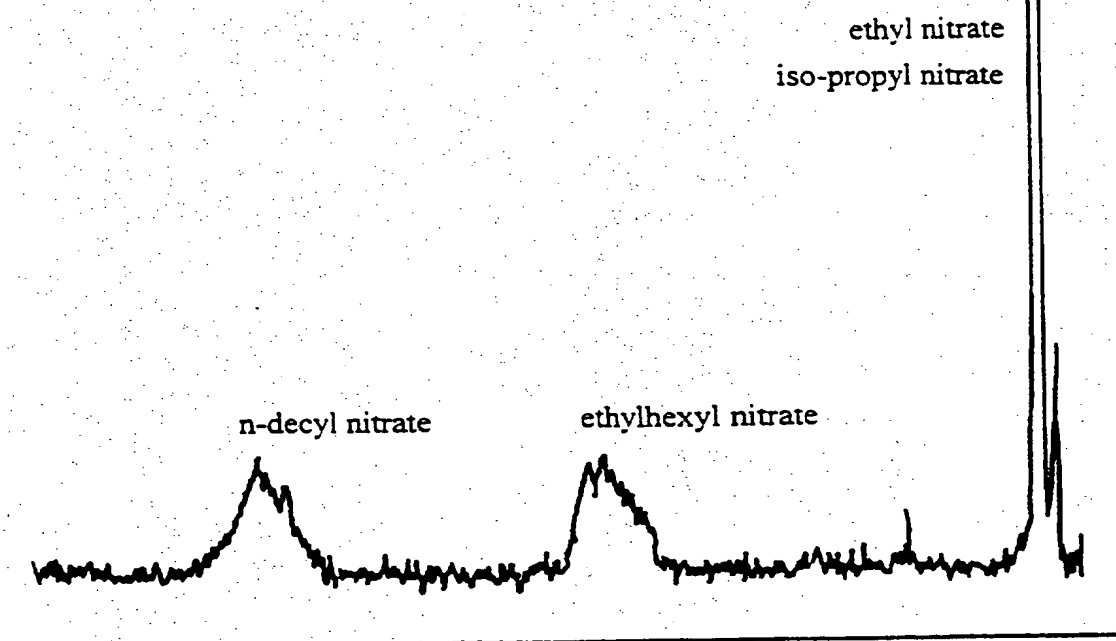


Figure 7

Method of Explosives Detection

This application relates to a method of explosives detection which is based on the technique of chemiluminescence and to an apparatus suitable for carrying out the method.

The technique of chemiluminescence has been employed in determining the concentration of constituents in gaseous sample mixtures. The technique depends on measuring the chemiluminescence generated during reaction of the constituent and an introduced reactant. For example the concentrations of both nitrogen oxide and ozone in gaseous mixtures have been determined by measuring the chemiluminescence produced by the reaction between these two compounds. To do this the mixture containing one of these target species is blended with a known quantity of the other reactant in a well-stirred reactor at relatively low pressures of one Torr or less and the emitted light is detected by, for example a suitable photomultiplier tube and associated current measuring device.

In a particular application of the above general methodology, the phenomenon of chemiluminescence has also been used in the detection of explosives through analysis of the vapours which are given off by such compounds. For example in the method of US patent 5,092,220, vapours of explosives materials are collected on surfaces coated with gas chromatograph material which trap the explosives vapours but repel nitric oxide. In this way extraneous nitric oxide is eliminated from the sample. The sample vapours are then desorbed and concentrated in one or more cold spot concentrators, after which different vapours are separated by high speed gas chromatography. The individual sample vapours are then decomposed in a pyrolyzer to generate nitric oxide which is fed to a chemiluminescence NO detector where it is mixed with ozone and the resultant radiation detected by a photodetector. The detector is operated at a pressure of 1-2 Torr.

This chemiluminescent equipment is known on the market as a Thermal Energy Analyser (TEA) and the combined system with the gas chromatograph used to give separation of mixtures whose components are to be detected is termed a GC/TEA system.

It will be appreciated that the GC/TEA system described here is quite elaborate and costly to implement. Moreover the chemiluminescent emission for the NO/O_3 reaction is in the very near IR region of the spectrum and a number of other chemiluminescent reactions occurring between small molecules which may be present, for example CO, give rise to similar emissions. Consequently spectral filtering has to be employed and the sensitivity of the equipment is reduced.

The aim of the present invention is to provide a method of explosives detection which utilises chemiluminescence while avoiding some of the disadvantages of the prior art systems, in particular their limited selectivity and the complexity of the apparatus involved.

To achieve this, the method of this invention makes use of the earlier observation of Gray and Yoffe (Proc. Royal Soc. A, 200, 1949, pp 114-124) that very dilute mixtures of alkyl nitrate vapours with an inert gas such as argon, emit a blue glow when heated under reduced pressure. The effect was observed over the temperature range 300-500°C and at pressures of up to about 30 kPa.

The applicant has now appreciated that, employing the phenomenon described by Gray and Yoffe, it is possible to devise a method of detection which relies on the direct chemiluminescent emission of heated molecules of energetic materials such as explosives and propellants without the need to provide any external energetic species to aid the chemiluminescent emission. In consequence of this the method of the invention demonstrates a higher degree of selectivity than prior methods with the possibility of eliminating altogether the need for chromatographic separation prior to admission of samples to the chemiluminescent detector. Additional advantages over the indirect methods which have been previously employed are, firstly, that with

emission in the blue region of the spectrum, detection of emission is much less affected by thermal noise than is the near IR emission from the NO/O₃ reaction. Secondly, the highly specific nature of the effect greatly reduces the need to filter light passing into the photomultiplier and thirdly, a detector employing this principle of operation can be made smaller, more robust and much less expensively than the current type of GC/TEA equipments.

Accordingly, the present invention provides a method for the detection of an energetic material in a sample to be tested which comprises introducing the sample into a chamber wherein the sample is heated while being maintained under a reduced pressure of less than 20 mbar, and detecting any light emitted.

In a preferred method of operation the sample is introduced into the heated chamber together with an inert gas, conveniently as the output from a gas chromatography apparatus.

In the process according to the invention the pressure of the sample (with or without inert gas) within the chamber is preferably maintained at not more than 10 mbar, most preferably around 2 to 3 mbar and the temperature of the mixture in the chamber will be at least about 200°C dependent upon the substance or substances to be detected. Preferably the temperature is of the order of 300°C to 500°C, most preferably around 400°C. It should be noted that the use of higher pressures than those mentioned will result in a progressive diminution of the amount of light which is generated and similarly at lower temperatures than those indicated. Whereas the effect of pressure is relatively independent of the material which is being detected however, the satisfactory temperature operating range varies with the material, ie its responsiveness and, at the higher end of the temperature range, its chemical stability. The above suggested operating temperatures are therefore given by way only of guidance and it will be necessary to determine an optimum temperature of operation for the detection of any particular substance. The means of such determination will be readily understood by those skilled in the art.

The inert gas to be used in the preferred method of the invention may be any of the inert gases in Group 8 of the Periodic Table such as helium or argon etc. but most conveniently nitrogen is used. The samples may be introduced either neat into the chamber or may be first dissolved in a solvent such as acetone, ethyl acetate, methanol or toluene, none of which themselves will produce any chemiluminescent emission under the conditions employed in the method according to the invention.

Alternatively, the apparatus of this invention will be connected downstream of a gas chromatography equipment such that the output from the latter is fed directly into the detector. In this way individual components of a mixture of substances can be sequentially detected as they exit from the chromatography equipment. In this mode of operation, in order to ensure that substances exiting the GC equipment are not condensed on the walls of the connector placed between the two equipments, it is preferred to provide a means of heating the connector. Typically the injection port into the chamber will be maintained at a temperature of 150°C to 250°C, most conveniently at about 170 to 180°C.

The process is applicable generally to the class of energetic materials, ie those materials which are capable of undergoing exothermic (energy-releasing) self-reaction on heating. It is in particular applicable to materials containing nitro-groups which constitute a large and important group of explosives and deflagrating materials. Thus the following substances have been detected using apparatus according to this invention:- IPN, NPN, EN, NG, diethylene glycol dinitrate (DEGDN), triethylene glycol dinitrate (TEGDN), glycerol mononitrate, glycerol-1,2-dinitrate, glycerol-1,3-dinitrate, propane-1,2-diol mononitrate, butane-1,2,4-triol trinitrate, 1,3-butane diol dinitrate, butane-2,3-diol dinitrate, erythritol tetranitrate (ETN), metriol trinitrate, pentane-2,3-diol dinitrate, 3-nitropentan-2-ol mononitrate, 2-ethylhexylnitrate, mannitol hexanitrate, 2-ethyl hexane-1,3-diol dinitrate, *n*-decyl nitrate, diethyl nitramine (DNA), dioxyethyl nitramine dinitrate (DINA), PETN and RDX. It must be stressed however that the above list is not to be regarded as being exhaustive with respect to those substances which may be detected using the method of this invention.

In another aspect the invention further provides an apparatus for the detection of energetic materials which comprises a chamber at least a part of one wall of which is transparent to visible radiation, heating means for said chamber, means for maintaining said chamber under reduced pressure, means whereby a sample may be introduced into said chamber, and means for detecting light emitted from the chamber through the said transparent part thereof.

Conveniently the chamber of the apparatus will be a cylindrical tube made of quartz which is sealed to an inlet for samples at one end and is open at the opposite end to a vacuum enclosure connected to an appropriate pumping system. A flat window is provided in the wall of the vacuum enclosure opposite an open end of the cylindrical chamber and on the other side of the window is placed a light detector of any convenient type, such as a photodiode, charge-coupled device or photomultiplier tube. The quartz tube forming the chamber is conveniently surrounded by an electrical heating coil to form a tubular furnace. A further inlet for the supply of eg. nitrogen gas to the chamber may be provided but alternatively the apparatus will be connected to the output from a gas chromatography equipment so as to provide detection of the separated components of a mixture passed from some outside source into the GC equipment as previously described.

In order to improve the selectivity of the photo detector, filters may be placed between the chamber and the photomultiplier tube, in particular to prevent longer wavelength IR radiation generated by the furnace passing through to the photomultiplier. Conveniently the window may itself comprise one of the filters.

In operation of the apparatus of the invention, the gas supply and heater (furnace) are switched on and allowed to stabilise. At the same time the light detection equipment, such as a photomultiplier, is switched on. Once the detector is ready a sample to be tested is injected into the chamber and any light emitted by the sample in the chamber is detected by the photomultiplier, the output from which may conveniently be recorded on a chart recorder or the like.

The amount of light generated by different substances has been found to vary with the amount of substance introduced into the chamber and the sensitivity of the detector is also some extent substance dependent. For example lower responses have been found for pentaerithritol tetranitrate (PETN) than for ethyl nitrate (EN), *n*-propyl nitrate (NPN), *iso*-propyl nitrate (IPN) or nitroglycerine(NG). Response is better at lower chamber pressures and pressures of less than about 9 mbar, most preferably of the order of 2 -3 mbar, have been found to be advantageous.

Where the detector is connected downstream of a gas chromatographic equipment, some trialling will be required to determine for each substance the preferred operating conditions and in the case of mixtures of substances, conditions which are a compromise between those most appropriate to the various substances in the mixture may have to be selected.

The invention will now be further described with reference to the following examples and to the accompanying drawings in which:

Figure 1 is a schematic representation of an apparatus according to the present invention connected downstream of a gas chromatography apparatus;

Figure 2 shows in greater detail an apparatus which is broadly similar to that of Figure 1; and

Figures 3 to 8 are traces of the output from the photomultiplier showing peaks corresponding to various substances injected into the apparatus of the present invention.

In Figure 1, a detector according to the present invention is shown generally at 1. It comprises a chamber 2 for the receipt of samples through input 3, the chamber comprising a quartz cylindrical tube 4 which is sealed to the inlet 3 at one end and is open at its other end to a vacuum chamber 5. Chamber 5 is evacuated through outlet 6

by a pump (not shown) and has, in its wall 7 lying opposite the end of tube 4, a window 8 which is transparent to visible light. Surrounding the tube 4 is an electrical heater coil 9, the leads to which are not shown.

A photomultiplier unit 10 is attached to the outside of the vacuum chamber in a position in line with the chamber 2 such that any emission of light within the chamber can be detected by the photomultiplier. Optical and IR filters are placed between chamber 2 and photomultiplier 10. Conveniently one such filter also forms the window 8, in the case of Figure 1 this is the IR filter and numeral 11 represents an optical filter. Photomultiplier 10 is provided with output leads to an amplifier and chart recorder (not shown) to record electrical output corresponding to light emissions in chamber 2.

In the apparatus of Figure 2, a cylindrical quartz tube 21 is located within a vacuum chamber 22 and is sealed to an inlet 23 at one end. In this case the inlet is for substances to be detected in the gas phase after passing through a gas chromatography apparatus. The interface connector 24 between the two apparatus is surrounded by a heated block 25 to obviate the possibility of substances in the gas stream from condensing out on a cold wall. Leads for the electrical heating wires to a resistance heater (not shown) surrounding the tube 21 are at 26. In this embodiment of the invention the photomultiplier tube has IR and visible filters 27 which are separate from the window 28 in the wall of the vacuum chamber 22. The filters are air cooled through inlets one of which is shown at 29.

Example 1

Using an apparatus which was generally similar to that illustrated in Figure 2 but in which the quartz tube also served as the vacuum chamber and was connected downstream of a gas chromatography apparatus, samples of glycerol-1,3-dinitrate, nitroglycerine, glycerol-1,2-dinitrate and ethylhexane-1,3-diol dinitrate in various solvents and in the amounts shown in Table 1 were introduced into the heated chamber. The carrier gas pressure varied between 0.2 and 2 bar for the various

samples while the chamber temperature was 400°C. The vacuum as measured by Pirani gauge was in the range 2.0 to 3.0 mbar. The connector was maintained at a temperature of around 175°C in each case. Use of different amounts of various samples shows the variations in responsiveness of the detector. The photomultiplier outputs for the various samples are shown in Figures 3 to 6.

Table 1

Spectrum no. (Figure ref.)	Compound	Solvent	Amount of solution
3(a)	Glycerol-1,3-dinitrate	Ethyl Acetate (1.5% solution)	1 µl
3(b)	"	"	5µl
4	Nitroglycerine	Methanol (1% solution)	1µl
5(a)	Glycerol-1,2-dinitrate	Ethyl acetate (1% solution)	1µl
5(b)	"	"	5µl
6	Ethylhexane-1,3-diol dinitrate	Acetone (2.6% solution)	5µl

Example 2

The same apparatus as used in Example 1 was connected to a GC apparatus and used to detect individual components of specimen mixtures fed to the GC apparatus. The following mixtures were used:-

- a) EN, IPN, ethylhexyl nitrate and *n*-decyl nitrate; and
- b) NG, erythritol tetranitrate, mannitol hexanitrate and metriol trinitrate.

A carrier pressure of 2.0 bar of nitrogen was used and the interface block was maintained at a temperature of 185°C. The initial GC oven temperature was 40°C. As shown in the trace at Figure 7, the IPN and EN peaks appeared immediately following injection, whereas the ethylhexyl nitrate peak appeared later as the GC oven temperature reached 65°C and the least volatile *n*-decyl nitrate later still when the oven temperature had reached 110°C. In the case of mixture (b) (trace at Figure 8) conditions were similar to those for (a) except that the initial GC oven temperature was 80°C.

Claims

1. A method for the detection of an energetic material in a sample to be tested which comprises introducing the sample into a chamber wherein the sample is heated while being maintained under a reduced pressure of less than 20 mbar, and detecting any light emitted.
2. A method according to claim 1 wherein the chamber is heated to a temperature of from about 300°C to about 500°C.
3. A method according to claim 1 or claim 2 wherein the pressure within the chamber is maintained at or below 10 mbar.
4. A method according to claim 3 wherein the pressure within the chamber is maintained at about 2 to 3 m bar.
5. A method according to any one of the preceding claims wherein an inert gas is introduced into the chamber together with the sample to be tested.
6. A method according to claim 5 wherein the sample is carried in an inert gas stream into the chamber.
7. A method according to claim 6 wherein the sample and gas stream comprise the output from a gas chromatography apparatus.
8. A method according to any one of claims 5 to 7 wherein the inert gas is selected from helium, argon or nitrogen.
9. A method according to any of the preceding claims wherein the energetic material to be detected is an explosives material.

10. Apparatus for the detection of energetic materials in a sample which comprises a chamber at least a part of one wall of which is transparent to visible radiation, means for heating said chamber, means for maintaining said chamber under reduced pressure, means whereby the sample may be introduced into the chamber, and means for detecting light emitted from the chamber through the said transparent part thereof.
11. Apparatus according to claim 10 and further comprising means for providing a gas supply to the chamber either in conjunction with or separately from the sample.
12. Apparatus according to claim 11 wherein the means for providing a gas supply and for providing a sample both comprise an inlet to the chamber connected to the output from a gas chromatography system.
13. Apparatus according to any one of claims 10 to 12 wherein the means for maintaining the chamber under reduced pressure comprises a vacuum chamber in communication with the chamber and a pump operatively connected thereto to maintain a reduced pressure within said vacuum chamber.
14. Apparatus according to any one of claims 10 to 13 wherein the light detecting means comprises a photomultiplier, photodiode or charge-coupled device.
15. Apparatus according to claim 14 wherein the light detecting means is operatively connected to a recording device such as a chart recorder.
16. Apparatus according to claim 10 wherein a filter is provided between the chamber and the light detection means in order to remove extraneous infra-red radiation from the light transmitted to the light detection means.
17. Apparatus as hereinbefore described and with particular reference to the accompanying drawings.



Application No: GB 9612241.1
Claims searched: 1 - 17

Examiner: Michael R. Wendt
Date of search: 21 August 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): G1B (BAA, BBC, BBG, BCC) ; G1A (AKA)

Int CI (Ed.6): G01N 21/71, 21/76, 33/22

Other: Online: WPI, Claims, Japio, Analytical Abstracts

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2016679 A (BOC) e.g. see Figs. Claim 1. Page 2 lines 11 - 15, 51 - 54 & 70 - 72.	10, 11, 13, 14.
X	GB 1511286 (P. BRASIL) e.g. see Figs. 2 & 3. Page 2 line 112 to page 3 line 60.	10, 11, 13, 14
A	US 5092218 (THERMEDICS) e.g. see Claims.	1

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